

AD-A158 534

DISTIBINES NEW ONE-DIMENSIONAL MATERIALS(U) MICHIGAN  
UNIV ANN ARBOR DEPT OF CHEMISTRY A J ASME 17 MAY 85  
AFOSR-TR-85-0502 AFOSR-81-0009

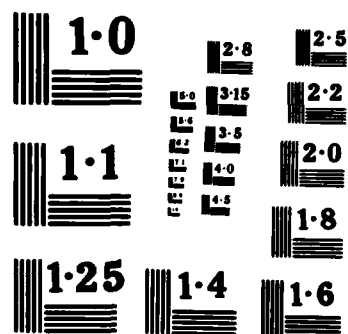
1/1

UNCLASSIFIED

F/G 7/3

NL





NATIONAL BUREAU OF STANDARDS  
MICROCOPY RESOLUTION TEST CHART

MAY 21 1985

Unclassified  
SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; Distribution unlimited		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR- 85-0502		
6a. NAME OF PERFORMING ORGANIZATION University of Michigan		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR/NC		
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry, University of Michigan, Ann Arbor, MI 48109			7b. ADDRESS (City, State, and ZIP Code) Building 410, Bolling AFS, D.C. 20332-6448		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION AFOSR		8b. OFFICE SYMBOL (If applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-81-009		
8c. ADDRESS (City, State, and ZIP Code) Building 410, Bolling AFB, D.C. 20332-6448			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2303	TASK NO. B2
			WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) Distibines, New One-Dimensional Materials					
12. PERSONAL AUTHOR(S) Dr. Arthur J. Ashe III					
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 6/1/81 TO 3/31/85		14. DATE OF REPORT (Year, Month, Day) May 17, 1985	
15. PAGE COUNT 17					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	distibines, diarsines, dibismuthines, heteroles		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) (a) A large number of novel diarsines, distibines and dibismuthines have been prepared. It has been shown that thermochromic distibines and presumably the corresponding dibismuthines show a solid-phase association which is responsible for the intense color of their solid state. Dibismuthines react with a variety of reagents. The products invariably involve cleavage of the metal-metal bond. A new general synthesis of C-unsubstituted heteroles has been developed.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS					
22a. NAME OF RESPONSIBLE INDIVIDUAL Anthony J. Matuszko			22b. TELEPHONE (Include Area Code) (202)-767-49		22c. OFFICE SYMBOL NC

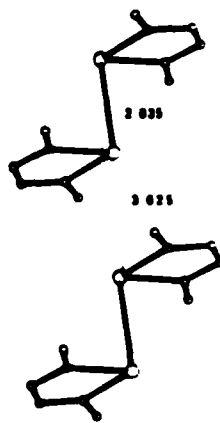
## DISTRIBUTION STATEMENT A

Approved for public release;  
Distribution UnlimitedDTIC  
ELECTE

AUG 29 1985

(b) Statement of Research Objectives.

Preliminary studies have demonstrated that 2,2',5,5'-tetramethylbistibole (1) shows a solid phase stacking which is associated with the intense blue color of its crystalline state (see Figure 1).<sup>1,2</sup> On melting or dissolution the color changes to pale yellow. This property suggests that distibines may form a new class of one-dimensional materials, which may lend themselves to future technological uses.



**Fig. 1.** Crystal packing diagram of 2,2',5,5'-Tetramethylbistibolyl. Distances along the Sb-Sb...Sk-Sb chain are indicated.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



Our research plan has been to investigate the long known thermochromic tetramethyldistibine 2 in order to test the generality of the effect. In addition, we have attempted to prepare a series of novel distibines with structures which might allow solid phase stacking. These series contain compounds of varying steric and electronic demand. Thus we hoped to be able to define the requirements for thermochromic behavior.

This thermochromic effect may be a common property of diatomic-like compounds of the polarizable elements of the lower right-hand corner of the periodic table. To test this hypothesis we have

AIR FORCE OFFICE OF SCIENTIFIC AND TECHNICAL INFORMATION  
NOTICE OF REPRODUCTION RIGHTS  
This document is in the public domain in the United States of America.  
Approved for public release; distribution unlimited.  
MATTHEW J. KILMER  
Chief, Technical Information Division

Approved for public release.  
distribution unlimited

also prepared a number of diarsines, dibismuthines, dichalodrins and some mixed compounds.

(c) Status of Research.

(i) Tetramethyldistibine (2). We have obtained a crystal structure of tetramethyldistibine.<sup>3</sup> As we had previously hypothesized, the compound stacks very similarly to 1 (see Figure 2). The molecule adopts a staggered trans conformation about the Sb-Sb single bond. The Sb atoms are aligned in linear chains with alternating intramolecular Sb-Sb bonds and short "intermolecular" Sb...Sb separations. Independent work by Becker and coworkers has shown that the thermochromic tetrakis(trimethylsilyl)distibine 3 adopts a similar solid phase arrangement.<sup>4</sup> Thus it is highly probable that all thermochromic distibines show a similar type of association.

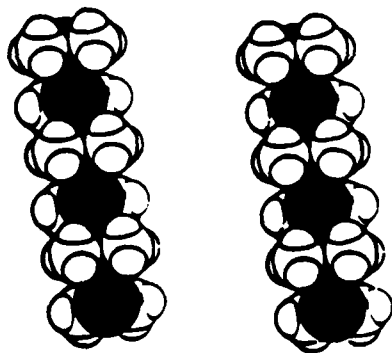
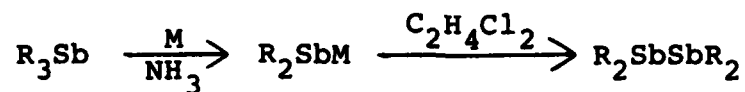
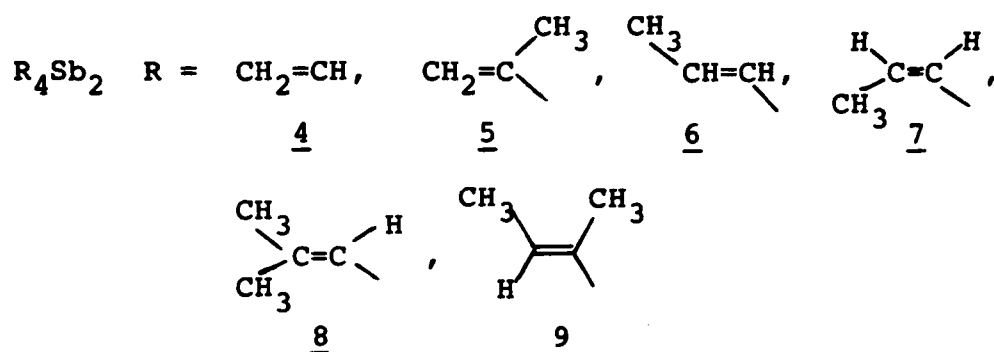


Fig. 2. Crystal packing drawing of the solid-state structure of tetramethyldistibine. Six molecules are illustrated in two chains. The bond distances are: Sb-Sb, 2.862(2), 3.628(1)Å; mean SbC, 2.15(2)Å. The bond angles are mean SbSbC, 93.6(6)°, mean CSbC, 93.5(15)°.

(ii) The Synthesis of New Distibines. We have explored a variety of literature methods for the preparation of distibines. In our hands the following procedure consistently gives yields of >80%:

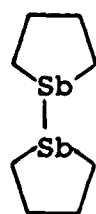
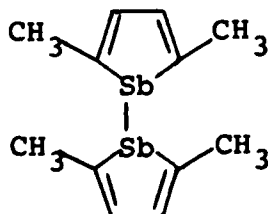
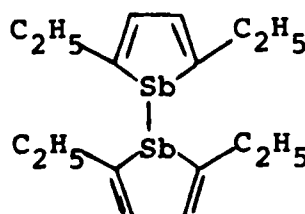
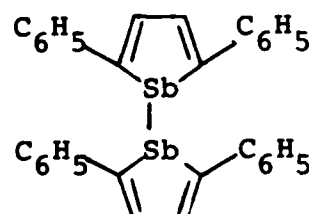
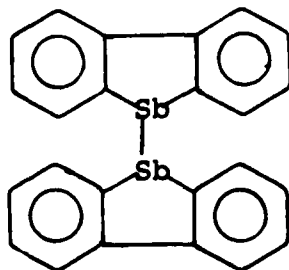
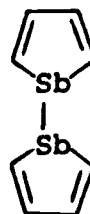


The new vinyl distibines (4-9) have been prepared:<sup>5</sup>



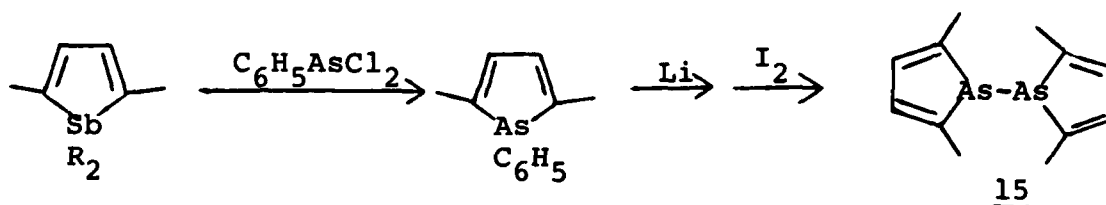
We were somewhat disappointed that only compounds 4 and 5 showed thermochromic properties. Although we had expected that intermolecular stacking might be sensitive to steric congestion, compounds 7 and 9 do not seem to be unduly congested. The structural requirements of thermochromic behavior seem very subtle.

We have also prepared a second series of distibines which are related to compound 1. The following five-membered ring compounds have been prepared:

10111121314

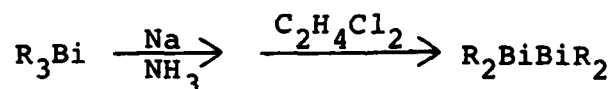
Distibines 10, 1 and 14 were thermochromic while 11, 12 and 13 were not. Obviously this series emphasized the need for sterically undemanding substituents on the five-membered ring.

(iii) Diarsines. 2,2',5,5'-Tetramethylbiarsole 15 was prepared by the indicated route:

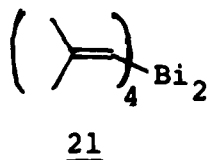
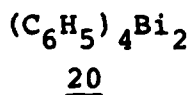
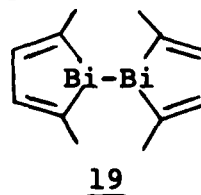
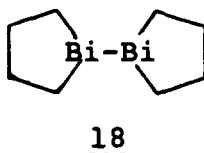
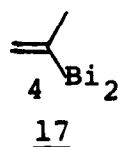
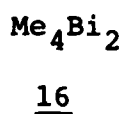


The diarsine is not thermochromic. A crystal structure of 15 indicates that it is not isostructural with 1, thus limiting the comparison of solid phase structures.<sup>6</sup> However, it is worth noting that no other diarsines have been shown to have thermochromic properties. For these reasons we have not further explored diarsines.

(iv) Dibismuthines. Prior to our work no well characterized dibismuthines had been reported in the literature. We find these materials are easily prepared even though they are very labile compounds:<sup>7,8,9</sup>



The following dibismuthines have been prepared:

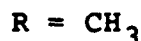
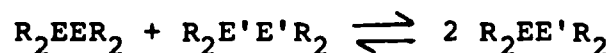


All dibismuthines have yellow-red liquid phases. Compounds 16-19 freeze to blue to blue-black solids, while 20 and 21 freeze to red liquids. Thus there is complete match of thermochromic properties of the dibismuthines with the corresponding distibines. The close analogy of the optical properties of solid dibismuthines with solid distibines strongly suggests similar solid-phase structures. We expect that the bismuth atoms of the thermochromic dibismuthines are aligned in linear chains with close intermolecular contacts. To date we have been unable to obtain a crystal structure in order to verify this prediction.

The colors of the solid dibismuthines 16-19 are red shifted relative to the corresponding distibines. This implies that dibismuthines have a relatively smaller band group.

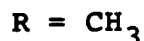
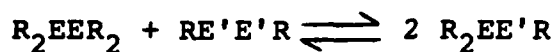
Since no chemical data are available on dibismuthines, we have undertaken a detailed study of the chemistry of tetramethyldibismuthine. The compound is sensitive to electrophilic, nucleophilic and free radical reagents. The products invariably result from cleavage of the metal-metal bond.

(v) Mixed Dipnictogens and Dichalcogen Compounds. We have found that mixed dipnictogens and dichalcogen compounds can be easily prepared:<sup>10</sup>



and

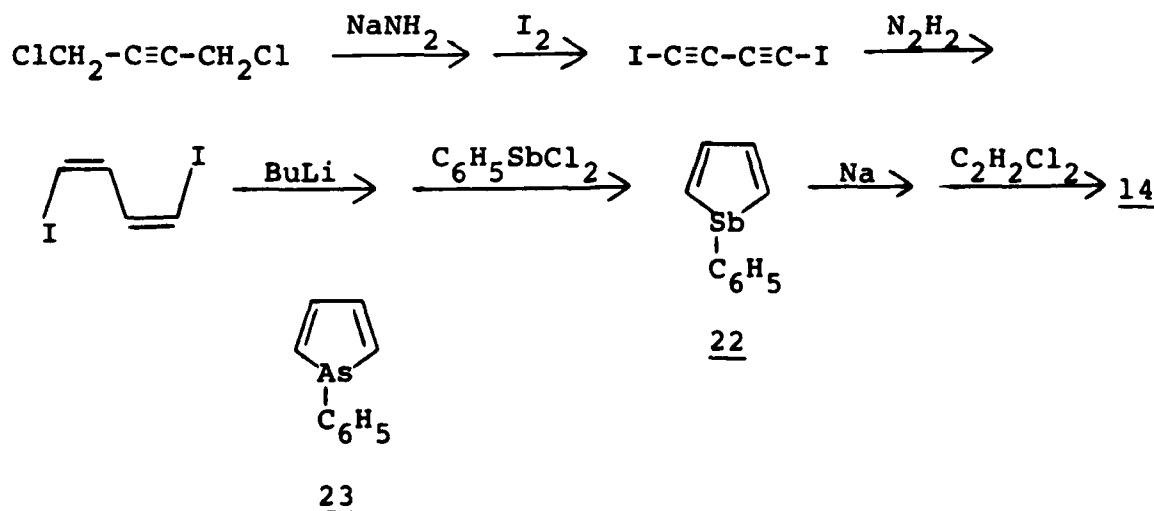




A large number of novel compounds have been prepared. Unfortunately the equilibria are very mobile, which has prevented us from isolating pure compounds in many cases. Thus it has been difficult to explore their thermochromic properties. On the other hand, these mobile exchange reactions appear to be a fruitful area for further research.

(vi) Synthesis of Pyrrole Analogs. The work outlined in section (ii) has demonstrated the great sensitivity of the thermochromic properties to steric bulk of the distibines. For this reason we felt it desirable to prepare the parent bistibole 14.

We have developed a novel synthesis of this compound as follows:<sup>11</sup>



This synthesis is important in that it constitutes the first general synthesis of C-unsubstituted heteroles. We have demonstrated the generality of the synthesis by also preparing arsenic compound 23. Pyrrole analogs 22 and 23 are potentially very important in tertiary concepts of aromaticity. This area seems worth further investigation.

#### Footnotes

1. Ashe, A.J. III; Butler, W.; Diephouse, T. R. J. Am. Chem. Soc. 1981, 103, 207.
2. Hughbanks, T.; Hoffmann, R.; Whangbo, M.-A.; Stewart, K. R.; Eisenstein, O.; Canadell, E. J. Am. Chem. Soc. 1982, 104, 3876.
3. Ashe, A. J. III; Ludwig, E. G., Jr.; Oleksyszyn, J.; Huffman, J. C. Organometallics 1984, 3, 337.
4. Becker, G.; Frendenblum, H.; Witthauer, C. Z. Anorg. Allg. Chem. 1982, 492, 37.
5. Ashe, A. J. III; Ludwig, E. G., Jr.; Pommerening, H. Organometallics 1983, 2, 1573.
6. Ashe, A. J. III; Butler, W. M.; Diephouse, T. R. Organometallics 1983, 2, 1005.
7. Ashe, A. J. III; Ludwig, E. G., Jr. Organometallics 1981, 1, 1908.
8. Ashe, A. J. III; Ludwig, E. G., Jr.; Oleksyszyn, J. Organometallics 1983, 2, 1859.
9. Ashe, A. J. III; Drone, F. J. Organometallics 1984, 3, 495.
10. Ashe, A. J. III; Ludwig, E. G., Jr., unpublished work.
11. Ashe, A. J. III; Drone, F. J. Organometallics, submitted (1985).

(d) Publications (Cumulative List):

(1) A. J. Ashe, III and E. G. Ludwig, Jr., Organometallics, 1, 1408 (1982): "A Reinvestigation of Paneth's Violet Compound. The Synthesis of Tetramethyldibismuthine."

(2) A. J. Ashe III, W. M. Butler and T. R. Diephouse, Organometallics, 2, 1005 (1983): "Synthesis and Molecular and Crystal Structure of 2,2',5,5'-Tetramethylbiarsolyl."

(3) A. J. Ashe III, E. G. Ludwig, Jr. and H. Pommerening, Organometallics, 2, 1573 (1983): "Synthesis and Spectra of Tetra-vinyldistibines."

(4) A. J. Ashe III, E. G. Ludwig, Jr. and J. Oleksyszyn, Organometallics, 2, 1859 (1983): "Preparation and Properties of Dibismuthines."

(5) A. J. Ashe, III, E. G. Ludwig, Jr., J. Oleksyszyn and J. C. Huffman, Organometallics, 3, 337 (1984): "The Structure of Tetramethyldistibine."

(6) A. J. Ashe III and F. J. Drone, Organometallics, 3, 415 (1984): "Synthesis of 2,2',5,5'-Tetramethylbibismole. A Thermochromic Distibine."

(7) A. J. Ashe III and F. J. Drone, Organometallics, submitted 1985: "Synthesis of 1-Phenylheteroles of the Group 5 Elements."

(8) A. J. Ashe III and E. G. Ludwig, Jr., manuscript planned: "Exchange Reactions of Dipnicogens and Dichalcogen Compounds."

(e) Professional Personnel:

(i) Dr. Arthur J. Ashe III, Professor of Chemistry, Principal Investigator.

(ii) Dr. Josef Oleksyszyn, Postdoctoral Research Associate (3/1/82-2/29/84).

(iii) Mr. Frederick Drone, Graduate Student, Research Assistant (6/82-present).

(iv) Mr. (now Dr.) Edward G. Ludwig, Jr., Graduate Student, Research Assistant until June 1984; 1984 Ph.D. Thesis, University of Michigan, "The Chemistry of Various Tetraorganodistibines and Tetraorganodibismuthines."

(v) Dr. Sultan Abu-Orabi, Postdoctoral Research Associate (June-August 1983).

(vi) Mr. Bryant Gilbert, Laboratory Assistant (June-July 1982).

(v) Mr. Daniel Szura, Graduate Student, Research Assistant (Summer 1984); M.S. 1985.

(vi) Mr Charles Kausch, Graduate Student, Research Assistant (June 1984-present).

(f) Papers Presented at Scientific Meetings (Cumulative List):

(i) A. J. Ashe III and T. R. Diephouse, "Proton NMR Spectra of Organobismuth Halides," 183rd National Meeting of the American Chemical Society, Las Vegas, Nevada, March 1982 (ORGN 075).

(ii) Arthur J. Ashe III, "Novel Heteroaromatic Compounds Containing Arsenic, Antimony and Bismuth," 14th Central Regional Meeting of the American Chemical Society, Midland, Michigan, June 1982.

(iii) A. J. Ashe III, E. Ludwig, Jr. and J. Oleksyszyn, "Thermochromic Distibines and Dibismuthines," 185th American Chemical

Society National Meeting, Seattle, Washington, March 1983 (INORG 202).

(iv) A. J. Ashe III and E. Ludwig, Jr., "Synthesis and Reactions of Dibismuthines," 186th American Chemical Society National Meeting, Washington, D.C., August 1983.

(v) Arthur J. Ashe III, "A Comparison of Diarsines, Distibines and Dibismuthines," XI International Conference on Organometallic Chemistry, Pine Mountain, Georgia, October 1983.

(vi) Arthur J. Ashe III, "Thermochromic Organometallics Containing Arsenic, Antimony and Bismuth," The Third Joint Meeting of the Great Lakes and Central Regions of the American Chemical Society, Kalamazoo, Michigan, May 1984.

(vii) Arthur J. Ashe III and E. G. Ludwig, Jr., "The Preparation of Mixed Tetraorganodipnicogen and Diorganodichalcogens," 188th American Chemical Society National Meeting, Philadelphia, Pennsylvania, August 1984.

(viii) Arthur J. Ashe III and F. G. Drone, "Synthesis of 1-Phenylheteroles of the Group 5 Elements," 189th American Chemical Society National Meeting, Miami Beach, Florida, May 1985.

(g) New Inventions on Specific Applications.

No patents have been applied for or issued.

**END**

**FILMED**

**10-85**

**DTIC**